The Critical Role of Phosphate in the Chemical Activation and Functionalization of Vanadium Phosphate Oxide for Selective Oxidation of *n*-Butane to Maleic Anhydride

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Computational details

The density functional calculations with periodic boundary conditions were performed using the Perdew-Burke-Ernzerhof (PBE) functional,[1] as implemented in the Quantum Espresso code. We used ultrasoft pseudopotentials (USPPs)[2] with a planewave basis set and a cutoff energy of 30 Ry for wavefunctions and 240 Ry for charge density. Electron smearing was employed using the Gaussian-smearing technique with a width of 0.01 Ry. For bulk structures, the Brillouin zone was sampled with 3×3×4 Monkhorst-Pack *k*-point grid[3] for α_1- and α_2-$VOPO_4$, and 2×2×2 for β-, X_1-$VOPO_4$ and $(VO)_2P_2O_7$. For slab calculations, the Brillouin zone was sampled with 3×3×1 *k*-point net for α_1- and α_2-$VOPO_4$ surfaces, and 2×2×1 for X_1-$VOPO_4$ and $(VO)_2P_2O_7$ surface. About 8 Å vacuum space between adjacent slabs was used to prevent the interaction between the replicas along the *z* direction. Transition states were located by using the "climbing-images" nudged elastic band (CI-NEB) method.[4,5] For most of the structures except different phases of $VOPO_4$ and the reactants of Figure 4 (a), (b), (c), (d), and (e), spin-polarized wavefunction is utilized. We also performed some calculations using the VASP code with the same *k*-point net to sample the reciprocal space, projector augmented-wave (PAW) pseudopotentials, and the setting PREC=ACCURATE. We calculated D_H's to be 49.9, 50.8, 52.1, 45.2, and 82.4 kcal/mol for O(1)

and O(2) on the α_I-$VOPO_4$ surface, and O(1) and O(2) on the α_{II}-$VOPO_4$ surface, and O(1)=P on the X_1-$VOPO_4$, respectively. Those numbers are similar to those obtained by the Quantum Espresso code with USPPs (48.5, 49.2, 52.1, 45.2, and 84.3 kcal/mol), indicating the use of USPPs gives essentially the same results as those using PAW.

In order to reduce the computational cost, we used the high pressure, high symmetry form of VOPO,[6] which has four molecular units per unit cell as compared to the ambient pressure, low symmetry form of VOPO with eight units.[7] We found that the band structures, projected density of states, and Mulliken charge distribution are very similar for the two forms, and hence we expect the surface chemistry to be similar.[8] Additionally since all the chemistry is initiated by the O(1)=P active site, we calculated the binding energy (D_H) of a free hydrogen atom to O(1)=P using the low symmetry, ambient pressure form of oxidized VOPO (X_1-$VOPO_4$) and compared the result to that using the high symmetry, high pressure form of oxidized VOPO. We found the two D_H's are quite similar (86.1 kcal/mol vs. 84.3 kcal/mol). As a result, we expect that the results based on the high symmetry form are similar to those that would be obtained using the low symmetry model.

Optimization of the cell parameters of $(VO)_2P_2O_7$ (0K) by the PBE functional leads to a = 7.624 Å, b = 9.661 Å, and c = 8.445 Å, in good agreement with experiment (a = 7.571 Å, b = 9.536 Å, and c = 8.362 Å at 300K) with deviations of 0.7, 1.3, and 1.0 %, respectively.[6] Since the atoms within the layers on the *bc* plane connect to adjacent *bc* layers through interlayer P-O-P bonds along the *a* direction, we expected that London Dispersion (van der Waals attraction) might play an important role. Therefore, we re-optimized the cell parameters with dispersion-corrected PBE (PBE-D2) functional[9] to obtain a = 7.447 Å, b = 9.558 Å, and c = 8.446 Å, which deviate from the experimental values by -1.6, 0.2, and 1.0 %, respectively. This shows that PBE-

D2 reduces the error in the calculated cell volume but that the error in the *a* parameter goes from +1.0% to -1.6%. We also re-calculated the reaction energy of atomic hydrogen to O(1)=P (which we identify as the active site for the VPO chemistry) using PBE-D2 leading to 87.5 kcal/mol for PBE-D2 compared to 84.3 kcal/mol for PBE. Thus, we conclude that the results from PBE are similar to those based on PBE-D2.

For small finite clusters, geometry optimizations were carried out using the same functional as implemented in the Jaguar code with the 6-31G** basis set[10,11] for all atoms except V. For V the first two shells of core electrons were described by the Los Alamos angular momentum projected effective core potential (ECP) using the double-ζ contraction of valence functions[12] (denoted as LACVP**).

Hydrogen absorption energy for estimating the reactivity of surface oxygen

The C-H activation powers of various lattice oxygen atoms can be evaluated quickly by simply calculating their binding energies to a free hydrogen atom (D_H).[13] The alkane C-H bond cleavage on the metal oxide surface usually proceeds through a hydrogen abstraction pathway, leading to the formation a surface O-H species and a weakly bounded alkyl radical. During this process, a C-H bond is broken and an O-H bond is formed. Since the strength of the C-H bond is a constant, the stronger the new formed O-H bond is, the more stable the product is, and according to the Hammond's postulate the smaller is the reaction barrier.

Stability of bulk $VOPO_4$

By comparing the energies of different phases of $VOPO_4$ to VOPO + $2\times O_2$(g), we find that the β-phase is the most stable with an energy -218.6 kcal/mol more stable than VOPO + $2\times O_2$(g). This is followed by α_{II}-phase (-211.2 kcal/mol) and then α_I (-193.4 kcal/mol). This order is consistent with experiments.[14] The proposed X_1-phase is only -49.6 kcal/mol downhill, corresponding to an adsorption energy of -24.8 kcal/mol per O_2(g). This suggests that it is a meta-stable state.

References

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Figure S1. The local environment of vanadium at different phases of $VOPO_4$ and VOPO. The blue polyhedron represents the VO_6 or V_2O_8 motif, while the yellow represents PO_4 or P_2O_7.

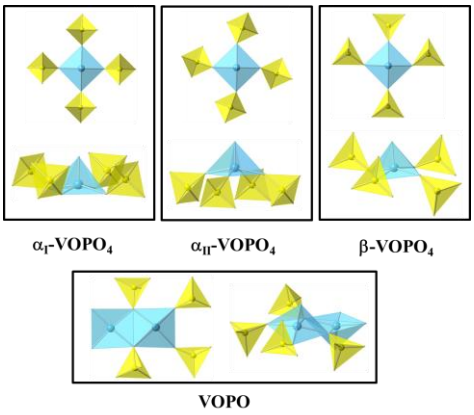


Figure S2. The local environment of phosphorus at different phases of $VOPO_4$ and VOPO. The blue polyhedron represents the VO_6 or V_2O_8 motif, while the yellow represents PO_4 or P_2O_7.

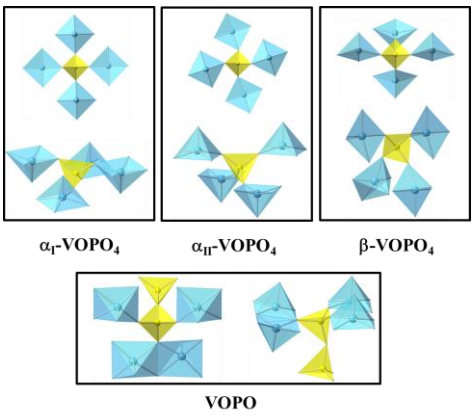


Figure S3. (a) α_I, (b) α_{II}, (c) β, and (d) X_1 phases of $VOPO_4$, which contain two, two, four, and eight formula units, respectively.

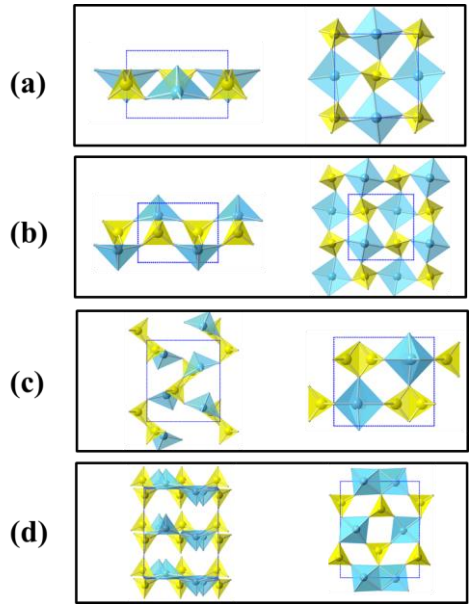
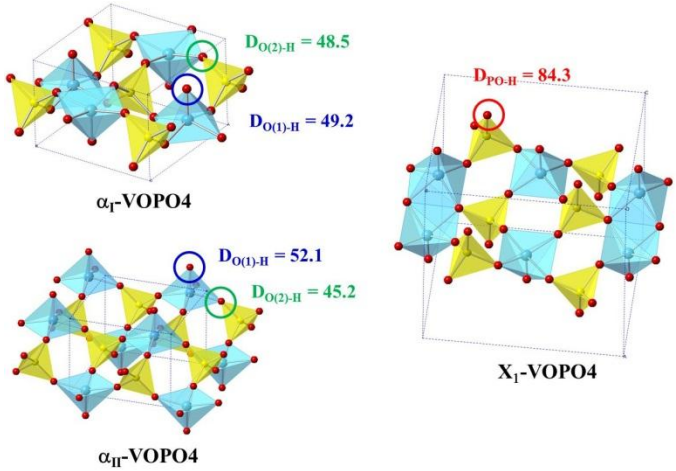
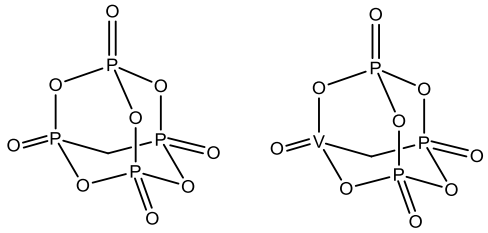


Figure S4. Crystal structures of the α_I-, α_{II}-, and X_1-$VOPO_4$ and the corresponding D_H's for their surface oxygen atoms.



Scheme S1



(a) **(b)**

4. Coordinates (fractional) and Energies (Hartree)

$(VO)_2P_2O_7$ bulk

a = 8.445 Å; *b* = 9.661 Å; *c* = 7.624 Å

E = -1206.793002 hartree

V	0.309641239	-0.002742885	0.036692923
V	-0.190323969	-0.497070037	-0.036455426
V	0.189537828	-0.497309982	-0.463833018
V	-0.309794141	-0.002943949	0.463231761
V	-0.309696210	0.002762114	-0.036693227
V	0.190312419	0.497083984	0.036376701
V	-0.189552348	0.497292806	0.463783752
V	0.309860779	0.002933927	-0.463162836
P	-0.002237998	-0.201920684	0.044216548
P	-0.502299119	-0.297930837	-0.044204631
P	0.502165281	-0.298169336	-0.455718052
P	0.002370410	-0.201528336	0.455503020
P	0.002154879	0.201929183	-0.044224397
P	0.502262538	0.297936060	0.044220653
P	-0.502133692	0.298148703	0.455728959

P	-0.002298121	0.201532507	-0.455509649
O	-0.318399086	-0.025452500	0.251723295
O	0.181236961	-0.474811930	-0.252291418
O	-0.181829727	-0.474353884	-0.247886806
O	0.318251996	-0.025200301	0.248180370
O	0.318370241	0.025413785	-0.251648908
O	-0.181310901	0.474765466	0.252304202
O	0.181736839	0.474373319	0.247843700
O	-0.318303954	0.025233513	-0.248176998
O	0.000013100	-0.169456345	0.249827915
O	-0.499651023	-0.329798238	-0.249909719
O	-0.000122543	0.169460577	-0.249832398
O	-0.500320599	0.329779950	0.249923267
O	-0.156157516	-0.147163514	-0.031463135
O	0.343663577	-0.352901083	0.030823871
O	-0.343993608	-0.353399748	0.468844181
O	0.156373028	-0.146805467	-0.468975262
O	0.156131604	0.147196302	0.031458582
O	-0.343624490	0.352886272	-0.030835471
O	0.344074888	0.353493568	-0.468823713
O	-0.156214136	0.146715581	0.468825711
O	-0.145754844	-0.135295116	-0.468172209
O	0.353747966	-0.364536066	0.468485484
O	-0.354306490	-0.364495695	0.032231639
O	0.145857548	-0.135473496	-0.032057409

O 0.145925868 0.135415175 0.468281012

O -0.353673610 0.364438311 -0.468481909

O 0.354340890 0.364502493 -0.032217914

O -0.145879016 0.135457299 0.032082162

O -0.500084778 -0.136171808 -0.021229322

O 0.000042156 -0.363724671 0.021648203

O 0.000194462 -0.363180364 0.478065413

O 0.500005548 -0.136384491 -0.478752656

O 0.500051266 0.136173047 0.021253946

O -0.000113234 0.363737575 -0.021690567

O -0.000167727 0.363192859 -0.478095206

O -0.500080433 0.136366389 0.478784987

$(VO)_2P_2O_7$ Surface

a = 8.362 Å; *b* = 9.536 Å; *c* = 19.994 Å

E(SCF) = -1241.25144541 hartree

V 0.305808114 0.011586039 0.403941808

V 0.187926530 -0.496873926 0.598448283

V -0.307583601 0.010837797 0.634883364

V -0.189739445 -0.495933378 0.439376462

V -0.311614839 0.003958437 0.439645815

V -0.194344110 -0.489227697 0.634946086

V 0.309903605 0.003448509 0.598841681

V 0.192595121 -0.488601481 0.402918945

P -0.008276904 0.209222092 0.392462452

P	-0.496508973	0.302541651	0.598299499
P	0.006446869	0.208603989	0.646357717
P	0.494759037	0.303159619	0.439386603
P	0.003522296	-0.197156947	0.439534049
P	0.491301275	-0.291563057	0.645879824
P	-0.005656955	-0.197848919	0.598526756
P	-0.493316933	-0.290465472	0.392287863
O	-0.298440967	0.043714009	0.713652940
O	-0.175600730	0.153794105	0.409693353
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O	-0.498368141	0.140056388	0.426730969
O	-0.189189456	0.492153204	0.519767169
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O	-0.359965542	0.377790599	0.411094995
O	0.009070498	0.373437464	0.630111401
O	0.295779927	0.044684407	0.325203613
O	0.173750690	0.152755318	0.629365092
O	0.125639699	0.136646557	0.431443566
O	0.496968850	0.139521920	0.611319934
O	0.187182473	0.491267111	0.518042489
O	0.335851596	0.352191765	0.411692673
O	0.358222263	0.376983019	0.626776981
O	-0.010877472	0.374413517	0.407967886
O	0.310233623	-0.007927181	0.518409355
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O	0.139739723	-0.123196524	0.626715683
O	-0.490945051	-0.125658822	0.408577272
O	0.202454676	-0.455925615	0.324160617
O	0.324369367	-0.347049216	0.628141203
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O	0.001149568	-0.360796891	0.611757279
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O	0.488923634	-0.126462635	0.630061807
O	-0.204459054	-0.457129997	0.713754925
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O	-0.002902966	-0.359992513	0.426109086
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O	-0.001975584	-0.177051154	0.519066359
O	-0.482025059	-0.303480622	0.724123756
O	0.479314999	-0.300974321	0.314027723
H	-0.381823716	-0.355726554	0.734782842
H	0.379421699	-0.353504123	0.303242411
H	-0.122018219	0.145159709	0.734956293
H	0.120427617	0.144789288	0.304093190

Hydrogen binds with O(1)=V on $(VO)_2P_2O_7$ Surface

a = 8.362 Å; *b* = 9.536 Å; *c* = 19.994 Å

E(SCF) = -1241.843136 hartree

V	0.303090050	0.011853914	0.401544547
V	0.189473357	0.503866802	0.596603044
V	0.691178967	0.009562338	0.633388270
V	0.806963536	0.504726449	0.437601931
V	0.685157814	0.004127305	0.438288642
V	0.803577994	0.508872552	0.618134933
V	0.308167342	0.002302816	0.597978143
V	0.189179607	0.512402217	0.402236004
P	0.989697361	0.209875517	0.392089530
P	0.500306307	0.300110458	0.595872432
P	0.004714267	0.210197563	0.645037379
P	0.491658950	0.302961226	0.436895106
P	-0.000098333	0.804764810	0.437712086
P	0.492167997	0.707601744	0.644442089
P	0.993348980	0.803121175	0.595952551
P	0.502389611	0.710339572	0.390776987
O	0.701705645	0.043706358	0.712084157
O	0.823345079	0.154518940	0.410711847
O	0.872424937	0.134779936	0.606155353
O	0.499078436	0.140076092	0.423692983
O	0.809280686	0.489641953	0.519747679
O	0.659861182	0.350557793	0.622376580

O	0.637986914	0.377703371	0.409594839
O	0.012260015	0.373032407	0.626825292
O	0.292219204	0.044691120	0.322812717
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O	0.125409637	0.137361557	0.429995858
O	0.495150020	0.137886790	0.609965879
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O	0.334079528	0.353391198	0.408560777
O	0.355480814	0.374097180	0.624839664
O	0.987881427	0.374834782	0.407558763
O	0.307245401	0.992836730	0.517435504
O	0.158548946	0.853344713	0.409537354
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O	0.834627620	0.850623590	0.624615835
O	0.854092536	0.877893384	0.408714580
O	0.486175296	0.873825485	0.629548799
O	0.791371883	0.545971614	0.709902603
O	0.669220804	0.653892259	0.407888165
O	0.619444415	0.638263330	0.600764493

O	0.993460065	0.641165727	0.426476421
O	0.965887162	0.209311270	0.723052323
O	0.014423230	0.197177889	0.313750372
O	0.493447276	0.321544483	0.516498236
O	0.995501650	0.830900226	0.516792840
O	0.533235206	0.692577219	0.720813742
O	0.474229278	0.699323086	0.312594139
H	0.637227848	0.635613724	0.726249612
H	0.372462615	0.649138960	0.302278920
H	0.872536999	0.146833282	0.732609600
H	0.114335243	0.144586413	0.302880126
H	0.835283081	0.477018092	0.741156486

Hydrogen binds with O(2) on $(VO)_2P_2O_7$ Surface structure (a)

a = 8.362 Å; *b* = 9.536 Å; *c* = 19.994 Å

E(SCF) = -1241.783285 hartree

V	0.306065902	0.011940403	0.404406462
V	0.186117461	0.507794404	0.598823638
V	0.691855767	0.008741701	0.630188143
V	0.811039082	0.503451053	0.440345390
V	0.688321679	0.003206455	0.441349047
V	0.810508382	0.516370466	0.623550751
V	0.306308890	-0.001602584	0.598279113
V	0.191779980	0.513371291	0.405317622
P	0.991864992	0.209206937	0.393727808

P	0.485920122	0.296295769	0.597365623
P	0.004391261	0.210058945	0.642129079
P	0.494952966	0.303494829	0.440221575
P	0.005161728	0.804383442	0.440975823
P	0.494797010	0.707712636	0.644052602
P	0.995650309	0.805482139	0.599543568
P	0.506978803	0.709975175	0.393416728
O	0.697337199	0.057976230	0.708188932
O	0.824927658	0.153611557	0.411624803
O	0.869414113	0.140082334	0.602654548
O	0.499117331	0.140480346	0.431301356
O	0.811087347	0.487121780	0.523429437
O	0.648652632	0.346219352	0.633562003
O	0.638169777	0.376959127	0.411248287
O	0.010028028	0.374674442	0.626778934
O	0.299904718	0.048355784	0.325854133
O	0.170610219	0.151757869	0.625337602
O	0.126553333	0.136503450	0.432224856
O	0.487399679	0.136765981	0.609944506
O	0.190855410	0.495276421	0.518451007
O	0.333379831	0.352722387	0.416758112
O	0.350721315	0.375621504	0.628863977
O	0.990040632	0.374333188	0.409136150
O	0.307100380	0.983648530	0.518006663
O	0.162024991	0.853632110	0.411423735

O	0.138989564	0.877749812	0.630711489
O	0.509827956	0.875376619	0.408832858
O	0.203617554	0.543161615	0.326252175
O	0.324825666	0.652838070	0.630551346
O	0.371692918	0.638606904	0.432043341
O	0.004781261	0.642735838	0.611216025
O	0.685021136	0.989545501	0.522786692
O	0.836323180	0.850972268	0.628185716
O	0.858151542	0.876901724	0.413376984
O	0.488465304	0.873364167	0.629784543
O	0.785549630	0.534831877	0.705426987
O	0.673233510	0.653557450	0.411095226
O	0.620631980	0.636409353	0.600106741
O	0.999868305	0.641261974	0.430458193
O	0.972872249	0.198648020	0.720135594
O	0.018171429	0.196343181	0.315461220
O	0.510792824	0.331045323	0.522096299
O	1.003407353	0.831059703	0.520719745
O	0.535829676	0.691673704	0.720575699
O	0.479723969	0.697873823	0.315174266
H	0.637892816	0.633661072	0.726149781
H	0.379478022	0.645477175	0.304758131
H	0.874215112	0.141630195	0.729407136
H	0.119824727	0.146324901	0.304819677
H	0.644553387	0.334154282	0.682642123

Hydrogen binds with O(2) on $(VO)_2P_2O_7$ Surface structure (b)

a = 8.362 Å; *b* = 9.536 Å; *c* = 19.994 Å

E(SCF) = -1241.799212 hartree

V	0.307692717	0.014016841	0.405293070
V	0.188534419	0.507302917	0.598887561
V	0.695921413	0.007760595	0.629417751
V	0.812379423	0.505981630	0.440574740
V	0.690709964	0.006577550	0.440637182
V	0.806829437	0.515321688	0.631981608
V	0.314225583	-0.002391406	0.599695493
V	0.193562172	0.514967952	0.404359319
P	0.994804132	0.212186861	0.393941013
P	0.509854483	0.300434575	0.596160549
P	-0.003372659	0.214558953	0.651648765
P	0.497562354	0.306690343	0.437904579
P	0.004528954	0.806224067	0.438577944
P	0.495276542	0.707863904	0.646997315
P	0.996622354	0.804172383	0.597634226
P	0.507361731	0.712317477	0.394754882
O	0.704058973	0.050717596	0.709190693
O	0.827930214	0.157240410	0.412133917
O	0.888467877	0.132553765	0.605271422
O	0.504358208	0.143458426	0.428749224
O	0.814974085	0.488322310	0.521888874
O	0.661562180	0.353850143	0.627708103

O	0.643143159	0.380569137	0.409727911
O	0.012470294	0.375596640	0.633907607
O	0.300763750	0.050433868	0.326261544
O	0.179869083	0.160089473	0.643246563
O	0.128951403	0.140300995	0.433283895
O	0.499765483	0.138843905	0.607693605
O	0.191102456	0.490857739	0.517814234
O	0.338859015	0.355306381	0.410401556
O	0.353605047	0.362652866	0.627204915
O	0.992037882	0.377608079	0.408861921
O	0.308263144	0.991892018	0.518180867
O	0.162182925	0.854789149	0.409713347
O	0.139046806	0.879688818	0.628489952
O	0.509868047	0.877301705	0.410241316
O	0.203203918	0.550428379	0.325363235
O	0.327246740	0.649832515	0.632967944
O	0.371961129	0.640272009	0.433248101
O	0.004639807	0.641020326	0.608819365
O	0.691367567	0.992333831	0.522589396
O	0.837266189	0.848309830	0.626690200
O	0.858456488	0.879874735	0.410572050
O	0.490325088	0.872237587	0.629913587
O	0.799332269	0.551172597	0.711438093
O	0.673610783	0.656521931	0.413485605
O	0.624221719	0.635595045	0.605101220

O	0.997210279	0.642861499	0.427799605
O	0.951530664	0.199798032	0.727242389
O	0.022228751	0.197859398	0.315580487
O	0.502178422	0.334603963	0.518612083
O	1.003095150	0.831317045	0.518698662
O	0.530943887	0.698181399	0.724649749
O	0.482034909	0.699027306	0.316191581
H	0.634455598	0.647136881	0.733212069
H	0.379498878	0.649924978	0.305553229
H	0.847899827	0.139494581	0.731209792
H	0.124322908	0.147348141	0.305540246
H	0.258045978	0.249488241	0.641633852

O_2 binds with vanadium on $(VO)_2P_2O_7$ Surface

a = 8.362 Å; *b* = 9.536 Å; *c* = 19.994 Å

E(SCF) = -1273.179616 hartree

V	0.305560570	0.013311515	0.403289119
V	0.197943505	0.513859471	0.615152029
V	0.690547678	0.020833991	0.642767923
V	0.809371675	0.510180641	0.440677459
V	0.688009891	0.002245531	0.440726135
V	0.807728573	0.521610296	0.639046962
V	0.309384657	0.014568860	0.601495607
V	0.202495982	0.510134324	0.431704665
P	0.992518714	0.214291334	0.400361334

P	0.517937868	0.302969229	0.593509875
P	0.997809263	0.218528709	0.646749611
P	0.517475494	0.297370244	0.443391054
P	0.001142021	0.808500655	0.443233126
P	0.499912434	0.720755442	0.644096059
P	0.992431928	0.814080998	0.601030689
P	0.500643493	0.709513346	0.398596457
O	0.700279526	0.050032733	0.721529050
O	0.829772163	0.154159108	0.421134032
O	0.855562688	0.146002595	0.611798508
O	0.508474499	0.139661595	0.418948840
O	0.794694094	0.501225076	0.520321171
O	0.648722013	0.372158672	0.634144296
O	0.644960354	0.381483797	0.406331549
O	0.992151373	0.378160157	0.627014604
O	0.286732401	0.041372104	0.324695233
O	0.162125465	0.159870238	0.626598754
O	0.134725741	0.139770185	0.433139699
O	0.499086178	0.146747022	0.619551247
O	0.160641159	0.515616938	0.529075271
O	0.349601752	0.354904989	0.440852051
O	0.359155844	0.373815316	0.587808321
O	0.990507854	0.374570378	0.421142332
O	0.319093023	0.004436944	0.521382020
O	0.163238355	0.856325248	0.417557915

O	0.146264384	0.881157006	0.626825348
O	0.506324380	0.876128102	0.409093684
O	0.209407560	0.528599575	0.350316911
O	0.346568996	0.664067170	0.612593914
O	0.379988092	0.642775141	0.447087924
O	0.989966161	0.653724160	0.613367998
O	0.680688893	0.985486553	0.520469858
O	0.841728414	0.873177191	0.632590741
O	0.858734415	0.881773026	0.410745405
O	0.492957660	0.886541171	0.633660090
O	0.794495578	0.549825475	0.717743743
O	0.672382017	0.657545669	0.409984645
O	0.647385078	0.657732211	0.610272138
O	0.992731374	0.646665011	0.432238510
O	0.981589539	0.205586212	0.725463624
O	0.008449506	0.207990592	0.321345326
O	0.583601639	0.282945116	0.518450444
O	0.987586146	0.841189971	0.521753483
O	0.505929404	0.698155558	0.722388566
O	0.450471794	0.687759376	0.323449694
H	0.601676709	0.643781544	0.736529643
H	0.352016242	0.625346468	0.320690060
H	0.882259351	0.156284779	0.739248564
H	0.104909621	0.154878517	0.307192300

O 0.151494358 0.551866402 0.705472585

O 0.262384462 0.445830324 0.698581802

O_2H binds with vanadium on $(VO)_2P_2O_7$ Surface

a = 8.362 Å; *b* = 9.536 Å; *c* = 19.994 Å

E(SCF) = -1273.790463 hartree

V 0.307572091 0.014163252 0.401691318

V 0.188668879 0.513416454 0.610959062

V 0.688415538 0.021240716 0.642018978

V 0.811270430 0.510672309 0.441194170

V 0.688234622 0.002537751 0.441612306

V 0.801505168 0.523211145 0.639784734

V 0.306056075 0.018707542 0.602463897

V 0.200954529 0.508984061 0.425163130

P 0.992578991 0.213844934 0.399128884

P 0.516748538 0.304177999 0.592691483

P 0.995228182 0.221581557 0.648410126

P 0.518173502 0.298383892 0.442825860

P 0.004877153 0.807830684 0.443845404

P 0.490250858 0.721605831 0.642616238

P 0.992766309 0.814116222 0.602773833

P 0.502637766 0.709850463 0.397713113

O 0.699095651 0.048246184 0.721101400

O 0.831124516 0.154144567 0.421630574

O 0.856387538 0.147363143 0.612190876

O	0.508961259	0.140020353	0.418677400
O	0.798402084	0.503715027	0.521234397
O	0.648019151	0.371927161	0.633907548
O	0.646064186	0.382138382	0.405988147
O	0.988330495	0.383357888	0.630394019
O	0.288494129	0.040461493	0.323001727
O	0.160923119	0.166358993	0.628417493
O	0.136964684	0.141203788	0.430987084
O	0.497284520	0.148457384	0.619397777
O	0.156880881	0.511908249	0.527627545
O	0.350391454	0.355911562	0.439925661
O	0.359617186	0.376523250	0.585597029
O	0.991597244	0.374957346	0.418661554
O	0.313527425	0.006194092	0.522464211
O	0.164952087	0.857826315	0.417163710
O	0.140967676	0.887205614	0.630473738
O	0.507485404	0.876698105	0.408751567
O	0.212428649	0.525650040	0.344388408
O	0.333700109	0.668864955	0.612771972
O	0.378138063	0.642414767	0.443873449
O	0.993385590	0.653628061	0.618070705
O	0.678187183	0.986812298	0.521456106
O	0.836872875	0.870158148	0.630704463
O	0.860441862	0.881427033	0.413504391
O	0.488359104	0.887451210	0.634419335

O	0.785640026	0.553948700	0.718356750
O	0.673946251	0.658526381	0.410364071
O	0.637772315	0.657158098	0.609958591
O	0.997154498	0.646231243	0.430807493
O	0.975509927	0.207741107	0.726948972
O	0.004427793	0.205538504	0.319923535
O	0.584558814	0.283046663	0.517987607
O	0.996448396	0.834421285	0.523090134
O	0.491217482	0.692638779	0.721490827
O	0.458002544	0.690164778	0.321593516
H	0.590515409	0.642409990	0.735390631
H	0.361286236	0.627689119	0.316795586
H	0.877024763	0.155286927	0.739334656
H	0.101407462	0.154114482	0.305212516
O	0.172572473	0.547852473	0.724464398
O	0.268011312	0.438417689	0.693259713
H	0.257651544	0.614533562	0.738146180

O_2 dissociatively binds with vanadium atoms on $(VO)_2P_2O_7$ Surface

a = 8.362 Å; *b* = 9.536 Å; *c* = 19.994 Å

E(SCF) = -1273.245865 hartree

V	0.211081787	0.017049479	0.449294666
V	0.198725213	0.515900249	0.626627866
V	0.688794903	0.021644562	0.645018979
V	0.796121857	0.509231360	0.422512119

V	0.699685979	0.007493300	0.424150897
V	0.809025912	0.521894658	0.646887388
V	0.298752195	0.016063627	0.626159489
V	0.286025143	0.517992540	0.448604621
P	0.973456423	0.217067262	0.383268475
P	0.518508460	0.305599325	0.597340577
P	0.991209791	0.224139410	0.642230131
P	0.521348473	0.285970930	0.447320664
P	-0.022650204	0.785555111	0.446946806
P	0.505627794	0.724263506	0.642745860
P	0.979744121	0.804667093	0.597009969
P	0.523100251	0.716721590	0.380741483
O	0.698302419	0.046880673	0.723755506
O	0.816280760	0.139421679	0.369848777
O	0.843534665	0.152650841	0.611491128
O	0.536905914	0.142196483	0.416476015
O	0.778264213	0.514916313	0.501902735
O	0.649647933	0.375271683	0.637879529
O	0.616600244	0.390753516	0.405591494
O	0.988304983	0.385540638	0.623812212
O	0.285666734	0.035182303	0.374767518
O	0.148664727	0.167719910	0.614473014
O	0.053163608	0.151701589	0.447666108
O	0.497266361	0.151017549	0.623273245
O	0.159121149	0.540684062	0.511097092

O	0.344456949	0.329366889	0.451333911
O	0.361114948	0.383106956	0.592883822
O	0.941109675	0.373070738	0.396527288
O	0.338413112	0.039072192	0.511680915
O	0.154614673	0.827729620	0.450840536
O	0.136915983	0.882580462	0.592464410
O	0.557834394	0.872478139	0.393755402
O	0.211048695	0.534718029	0.374031691
O	0.348758786	0.667269439	0.614696638
O	0.444853034	0.651899646	0.445657650
O	1.000347515	0.650760327	0.623953377
O	0.713707618	1.008269631	0.503857932
O	0.848454993	0.875221938	0.637042626
O	0.882834401	0.893565853	0.406801816
O	0.508802626	0.885164890	0.623560315
O	0.799484465	0.546955210	0.725612036
O	0.678932425	0.637430074	0.366446822
O	0.654248079	0.652381315	0.613095972
O	0.959144560	0.643760904	0.414266134
O	0.986872874	0.211944117	0.721225921
O	0.087358711	0.210322940	0.321205894
O	0.589162165	0.287282994	0.522317443
O	0.910261620	0.783973389	0.522004506
O	0.507915720	0.713747500	0.721832039
O	0.406906276	0.710619556	0.319413018

H	0.599346572	0.659704830	0.739644735
H	0.318097292	0.640052221	0.327266668
H	0.893507790	0.159252281	0.738358471
H	0.176497451	0.139896458	0.328348866
O	0.217138190	0.493486350	0.704874601
O	0.280256599	-0.006766123	0.704394181

α_1-$VOPO_4$ bulk

a = 6.246 Å; *b* = 6.246 Å; *c* = 4.423 Å

E(SCF) = -317.7416348 hartree

O	0.500119279	0.701841490	0.294012908
O	0.499892484	0.298155581	0.294010938
O	0.798169418	0.000119597	0.294012991
O	0.201852375	0.999880000	0.294023159
O	0.999880324	0.798158286	0.705990845
O	0.000107337	0.201844669	0.705992728
O	0.701831151	0.499880471	0.705989792
O	0.298147185	0.500120046	0.705980117
V	-0.000011721	0.500000729	0.616318385
O	-0.000011666	0.499999250	0.257530309
V	0.500011912	-0.000000813	0.383631246
O	0.500011969	0.000000678	0.742512240
P	-0.000002121	-0.000001648	0.499996915
P	0.500002079	0.500001664	0.499997429

α_1-$VOPO_4$ surface

a = 6.246 Å; *b* = 6.246 Å; *c* = 12.145 Å

E(SCF) = -317.742408 hartree

O	0.517030000	0.692050000	0.265130000
P	0.516910000	0.490210000	0.340540063
O	0.516810000	0.289128078	0.264538423
O	0.815373757	-0.009527628	0.264412379
O	0.218447604	0.990263792	0.264426199
O	1.016798670	0.788762089	0.415813665
O	0.017005680	0.191719990	0.415879008
O	0.718549320	0.489879447	0.416141462
O	0.315265241	0.490088737	0.416136517
V	1.016903519	0.490235723	0.380757531
O	1.016899287	0.490213890	0.250944470
V	0.516905670	-0.009462075	0.299744854
O	0.516924593	-0.009329028	0.429542922
P	1.016895479	0.990327894	0.340127806

Hydrogen binds with O(1) on the α_1-$VOPO_4$ surface

a = 6.246 Å; *b* = 6.246 Å; *c* = 12.145 Å

E(SCF) = -318.3201147 hartree

O	0.517030000	0.692050000	0.265130000
P	0.516910000	0.490210000	0.341091692
O	0.516810000	0.291696613	0.266138636
O	0.815444487	-0.006521128	0.261107703

O 0.217237951 0.994340466 0.258391377

O 1.021515126 0.797662761 0.413263034

O 0.020777772 0.197795181 0.411078650

O 0.720454286 0.495413993 0.415968336

O 0.317385012 0.499155906 0.418130354

V 1.016785944 0.497206810 0.378025239

O 1.017885687 0.498581387 0.248123541

V1 0.515123142 -0.011565179 0.288877908

O 0.506228888 -0.019007684 0.433849241

P 1.017671513 0.996674705 0.335554889

H 0.433644987 0.857606114 0.468699539

Hydrogen binds with O(2) on the α_1-$VOPO_4$ surface

a = 6.246 Å; *b* = 6.246 Å; *c* = 12.145 Å

E(SCF) = -318.319053 hartree

O 0.505643439 0.690127267 0.259189723

P 0.527108514 0.490552202 0.329836480

O 0.505358259 0.291154403 0.258927573

O 0.809032620 -0.009184882 0.270479776

O 0.209847958 0.990192148 0.265451413

O 1.016886434 0.788515017 0.420050114

O 0.018016773 0.192237663 0.420144507

O 0.710132588 0.489654105 0.414366729

O 0.326491818 0.491619658 0.419463558

V 1.005775348 0.490334977 0.377970747

O	1.017771120	0.490345106	0.247987146
V	0.508466660	-0.009208863	0.301994807
O	0.503403122	-0.008535912	0.432533423
P	1.013059159	0.990381769	0.344177063
H	0.378616186	0.482125342	0.495276943

α_2-$VOPO_4$

a = 6.111 Å; *b* = 6.111 Å; *c* = 4.623 Å

E(SCF) = -317.748731 hartree

O	0.209587036	0.951127905	0.304388019
O	0.290412814	0.548875489	0.304385244
O	0.548875757	0.209589539	0.304387012
O	0.951123994	0.290414974	0.304387571
O	0.790413405	0.048868588	0.695615293
O	0.709586741	0.451128043	0.695618080
O	0.451127681	0.790410875	0.695616517
O	0.048872575	0.709584597	0.695615941
V	0.250001831	0.250004546	0.221315823
O	0.249999979	0.250003141	0.876818970
V	0.749998176	0.749995463	0.778718219
O	0.750000016	0.749996843	0.123149282
P	0.249999513	0.750000677	0.499998478
P	0.750000481	0.249999319	0.499985550

α_2-$VOPO_4$ surface

a = 6.111 Å; *b* = 6.111 Å; *c* = 15.762 Å

E(SCF) = -317.7462076 hartree

O	0.169030000	0.918500000	0.424140000
P	0.209450000	0.717380000	0.481563908
O	0.249860000	0.516299167	0.424024376
O	0.508456892	0.175038668	0.424115167
O	0.910424157	0.259818420	0.424117023
O	0.752145478	0.016363713	0.538907556
O	0.666730306	0.418396848	0.538905308
O	0.410538895	0.759785134	0.538901178
O	0.008331813	0.675057947	0.538895851
V	0.209444600	0.217397084	0.397045016
O	0.209419727	0.217433764	0.296873152
V	0.709433473	0.717354899	0.565985052
O	0.709411957	0.717388020	0.666138703
P	0.709454889	0.217355214	0.481485178

Hydrogen binds with O(1) on the α_2-$VOPO_4$ surface

a = 6.111 Å; *b* = 6.111 Å; *c* = 15.762 Å

E(SCF) = -318.3285407 hartree

O	0.169030000	0.918500000	0.424140000
P	0.209450000	0.717380000	0.481725757
O	0.249860000	0.517463251	0.423409802
O	0.510011335	0.174445219	0.426038162

O	0.910345296	0.260523237	0.426587811
O	0.755261056	0.017723283	0.542735992
O	0.662899367	0.417683413	0.541705784
O	0.410068084	0.762297225	0.539156523
O	0.007330934	0.670676568	0.538199946
V	0.209973454	0.217884538	0.397833913
O	0.209613189	0.218006707	0.297517493
V	0.709198500	0.716182726	0.568748380
O	0.709449531	0.713222474	0.679789754
P	0.709959278	0.216350499	0.483894744
H	0.686597070	0.574831617	0.709964435

Hydrogen binds with O(2) on the α_2-$VOPO_4$ surface

a = 6.111 Å; *b* = 6.111 Å; *c* = 4.623 Å

E(SCF) = -318.3175941 hartree

O	0.169030000	0.918500000	0.424140000
P	0.209450000	0.717380000	0.477798066
O	0.249860000	0.523249352	0.421131576
O	0.510801383	0.177007257	0.423471902
O	0.913891403	0.262725380	0.420667849
O	0.761382608	0.015608304	0.534903451
O	0.671635573	0.422763277	0.535807612
O	0.407017347	0.770227628	0.546621320
O	0.033745468	0.668118796	0.545112265
V	0.212763223	0.218707109	0.391855003

O 0.212775716 0.215160568 0.291628555

V 0.736316044 0.716668372 0.570443145

O 0.720776730 0.718842454 0.671098893

P 0.715219431 0.219490394 0.479104100

H 0.336781021 0.764307913 0.602761146

β-$VOPO_4$

a = 7.911 Å; *b* = 6.212 Å; *c* = 7.189 Å

E(SCF) = -635.5033472 hartree

O 0.129034516 0.550386121 0.240617852

O 0.370626487 0.449635910 0.740725304

O 0.870853143 0.050394042 0.759369529

O 0.629278329 0.949649363 0.259285709

O 0.870853146 0.449605975 0.759369529

O 0.629278326 0.550350662 0.259285709

O 0.129034516 0.949613893 0.240617855

O 0.370626489 0.050364112 0.740725307

V 0.174705151 0.250000007 0.227521187

P 0.878698548 0.250000008 0.887622469

O 0.720538994 0.250000012 0.019879261

O 0.044429719 0.250000007 1.000468565

O 0.362022466 0.250000007 0.146293867

V 0.325118087 0.750000011 0.727336747

P 0.621589280 0.750000012 0.387457884

O 0.779748560 0.750000009 0.519607870

O 0.455848108 0.750000013 0.500541150

O 0.137914718 0.750000013 0.645948661

V 0.825237259 0.750000008 0.772455191

P 0.121227622 0.750000008 0.112373417

O 0.279418823 0.750000010 0.980157724

O 0.955517111 0.750000009 -0.000519980

O 0.637920536 0.750000008 0.853697213

V 0.674848397 0.250000013 0.272694199

P 0.378346250 0.250000010 0.612538650

O 0.220205676 0.250000008 0.480364586

O 0.544107788 0.250000012 0.499483974

O 0.862064867 0.250000013 0.354061843

X_1-$VOPO_4$ bulk

a = 9.730 Å; *b* = 9.525 Å; *c* = 7.860 Å

E = -1270.737274 hartree

V 0.038716030 0.011352013 0.298320072

P 0.077861250 0.220516024 -0.014864081

O 0.284673759 0.001667515 0.703976768

O 1.013826981 0.146199333 0.824703862

O 0.513502591 0.142977540 0.822281233

O 0.975653837 0.132695681 0.485731967

V 0.537085934 0.509822736 0.203153112

P 0.406174179 0.285307117 0.481226434

O 0.786805324 0.502753648 0.797535585

O 0.481063750 0.365714411 0.636171437

O	-0.014734137	0.368991811	0.637865112
O	0.510358834	0.373463389	0.983895343
V	0.446907427	-0.006307189	0.703854983
P	0.576926489	0.217899546	0.982703653
O	0.200998226	0.003349410	0.296851728
O	0.502155990	0.137110662	0.136847495
O	1.002644474	0.140177217	0.139181067
O	0.472989500	0.130050162	0.483986968
V	0.949088501	0.496651835	0.797983006
P	0.909993473	0.288525605	0.483380482
O	0.699362777	0.502280201	0.202607522
O	-0.026472131	0.363617621	0.323418018
O	0.470300326	0.360695288	0.321849378
O	0.012179009	0.376401320	-0.013735584
V	0.948678095	0.997345611	0.704379318
P	0.909105103	0.788147915	1.017521050
O	0.699730907	1.001875921	0.297787171
O	-0.028089406	0.863157366	0.178274288
O	0.470124021	0.860693898	0.178507227
O	0.011820956	0.876470602	0.516577366
V	0.446557420	0.493276078	0.796299955
P	0.577188340	0.717794918	0.518527302
O	0.202018831	0.504536141	0.205032692
O	0.502192932	0.637205801	0.363943637
O	1.003892110	0.640727294	0.363461869
O	0.472635643	0.630229488	0.016294010

V 0.537413295 1.009397959 0.297410475

P 0.406223630 0.785723211 0.018340480

O 0.786427338 1.003956907 0.704314450

O 0.481619247 0.866082729 0.864129051

O -0.015468200 0.869185147 0.864059829

O 0.510891032 0.873445585 0.516692087

V 0.039741823 0.512385248 0.204013790

P 0.078261916 0.720933480 0.518771179

O 0.284298912 0.501334843 0.796059065

O 1.013758986 0.646020072 0.678109244

O 0.513683617 0.642637152 0.678474961

O 0.975957161 0.632807407 1.016175474

O 0.229213579 0.222678893 -0.003395144

O 0.255012448 0.282686109 0.492458494

O 0.255017955 0.783395102 0.006708790

O 0.229620806 0.723705593 0.508236947

O 0.728181725 0.221238281 0.994434885

O 0.728500081 0.720785178 0.506917379

O -0.241356974 0.285869372 0.494362557

O -0.242115722 0.784787794 1.004874563

Hydrogen binds with O(1)=P on the X_1-$VOPO_4$ bulk

a = 9.525 Å; *b* = 7.860 Å; *c* = 14.607 Å

E = -635.9855629 hartree

O -0.003530000 0.720820000 0.262740000

V 0.976240000 0.713440000 0.369718967

O	0.850020000	0.879882072	0.389463194
O	0.117934899	0.827783673	0.427159745
V	0.486333165	0.193133120	0.436208753
P	0.268965976	0.469116163	0.359448257
O	0.337620830	0.645817851	0.388404439
O	0.346796982	0.995406644	0.411368139
P	0.189986628	0.999184085	0.457307015
O	0.109869690	0.137913011	0.395123696
O	0.103570974	0.488829455	0.393331106
O	0.531424495	0.187928889	0.541056594
O	0.334757264	0.342596326	0.432329833
O	-0.058574569	0.274368749	0.519849711
O	0.837818670	0.186759733	0.349709920
V	0.461666986	0.812684244	0.354021600
P	0.682313666	0.520888241	0.428968931
O	0.609198107	0.363395849	0.389478224
O	0.607152579	0.019256143	0.373486957
V	-0.024643522	0.294501361	0.414401021
P	0.761642464	0.012349304	0.326125342
O	0.843134523	0.522061927	0.400205378
O	0.451568471	0.814523127	0.246473138
O	0.618515107	0.685394480	0.392606160
O	0.280365125	0.419699352	0.262365076
O	0.756739160	-0.031236946	0.228234842
O	0.193748371	1.033293365	0.556292688

O	0.676792876	0.521934873	0.537043964
H	0.642629980	0.415413139	0.565116627